

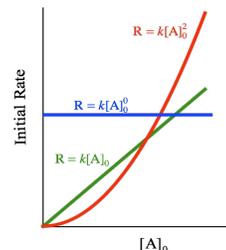
Topics:

1) **Reaction Rates** (The change in the concentration of substance per unit time)

- a) Determine the average rate of a reaction based on the change in conc. of a substance.  $Rate_A = \frac{\Delta[A]}{\Delta t}$
- b) Use stoichiometry to convert from the average rate of appearance/disappearance of one substance in a reaction to the average rate of appearance/disappearance of another substance in the reaction.
- c) The instantaneous rate of disappearance of a reactant is faster in the beginning of a reaction.

2) **Rate Laws:** For the reaction  $A + B \rightarrow C$  the general rate law is  $Rate = k[A]^x [B]^y$

- a) Use experimental data of concentrations and rates to determine the order with respect to any reactant.
- zero order—the rate does not change with change in concentration of substance.
  - first order—the rate doubles when the concentration of substance doubles
  - second order—the rate quadruples when the concentration of the substance doubles.
- b) Analyze graphs of Rate vs  $[A]_0$  to determine the order of that substance. See graph→



3) **Integrated Rate Laws:** (Rate Laws consisting of concentration, k and time)

- a) Zero order:  $[A]_t - [A]_0 = -kt$  Graph: **[A] vs time** is linear won't need half-life eq.

- a) First order:  $\ln[A]_t - \ln[A]_0 = -kt$  Graph: **ln[A] vs time** is linear  $Half\text{-}life = t_{1/2} = \frac{0.693}{k}$

- b) Second order:  $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$  Graph of  $\frac{1}{[A]}$  vs. **time** is linear *constant* won't need half-life eq

4) **Activation Energy, Collision Theory and the Arrhenius Equation**

- a) Use collision theory to explain why the rate of a reaction increases when one increases concentration of a reactant, increases surface area, increases temperature or uses a catalyst.
- b) Label energy diagrams: activation energy, activated complex, and  $\Delta H$
- c) Use Arrhenius equation to determine how temperature and  $E_A$  affects k (rate constant)

When T increases, k increases (rate also increases); When  $E_A$  is larger, k is lower (rate is also slower)

$$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \quad \text{Graph: } \ln k \text{ versus } 1/T \text{ is linear where } m = -\left(\frac{E_a}{R}\right)$$

- d) Compare and calculate rate constant (k) values at different temperatures →

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

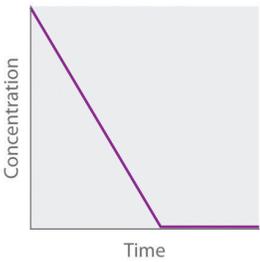
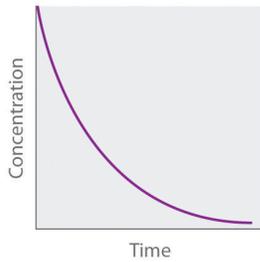
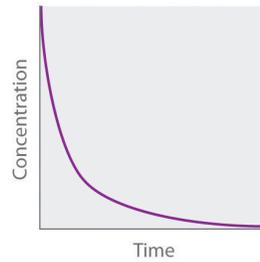
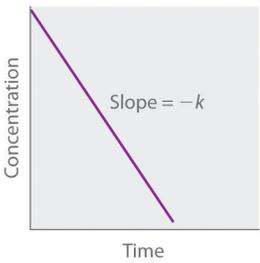
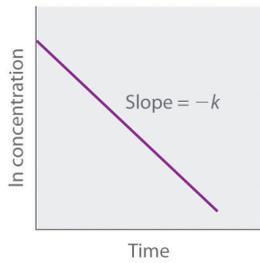
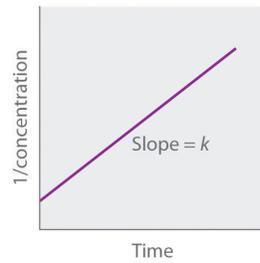
5) **Reaction Mechanisms:** (Rates of reactions can be used as evidence to support a reaction mechanism.)

- a) The rate determining step is the step in the mechanism with the highest activation energy. (slowest)
- b) The coefficients of the reactants in the rate determining step are the exponents in the rate law.
- If  $aA + bB \rightarrow cC$  is the rate determining step then the rate law is  $Rate = k [A]^a [B]^b$
  - This is because the rate of a rxn is dependent on the molecules colliding in the rate determining step.
  - If a reactant is not involved in the rate determining step, the rxn is zero order w/ respect to that reactant.

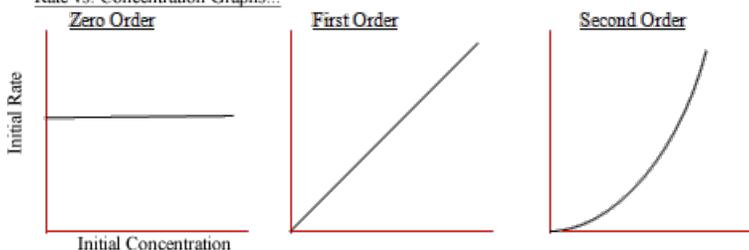
6) **Catalysts:** chemical substances that speed up the rate of a reaction without being consumed.

- Catalysts allow the reaction to proceed by a pathway (mechanism) that is more kinetically favorable, so the overall rate increases.
- Catalysts often lower the activation energy of the reaction and can also increase the frequency of collision.
- Catalysts are not consumed because they react and then they are regenerated.

# Summary of formulas and plots in Kinetics Unit

	Zeroth Order	First Order	Second Order																								
<b>Differential rate law</b>	Rate = $-\frac{\Delta[A]}{\Delta t} = k$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
<b>Concentration vs. time</b>																											
<b>Integrated rate law</b>	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
<b>Straight-line plot to determine rate constant</b>																											
<b>Relative rate vs. concentration</b>	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1</td> </tr> <tr> <td>2</td> <td>1</td> </tr> <tr> <td>3</td> <td>1</td> </tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1</td> </tr> <tr> <td>2</td> <td>2</td> </tr> <tr> <td>3</td> <td>3</td> </tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table border="1"> <thead> <tr> <th>[A], M</th> <th>Rate, M/s</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1</td> </tr> <tr> <td>2</td> <td>4</td> </tr> <tr> <td>3</td> <td>9</td> </tr> </tbody> </table>	[A], M	Rate, M/s	1	1	2	4	3	9
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<b>Half-life</b>		$t_{1/2} = \frac{0.693}{k}$																									
<b>Units of k, rate constant</b>	M/s	1/s	M <sup>-1</sup> ·s <sup>-1</sup>																								

Rate vs. Concentration Graphs...



## Initial Rate vs. Initial Concentration of a reactant.

- 0<sup>th</sup> order: initial rate is the same no matter what the initial concentration of reactant.
- 1<sup>st</sup> order: As the initial concentration of a reactant increases, the initial rate increases proportionately.
- 2<sup>nd</sup> order: As the initial concentration of reactant increases, the initial rate increases exponentially.